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PROPAGATION OF SUPERSONIC WAVES IN LIQUID MIXTURES AND INTERMOLECULAR FORCES: ETHER AND ACETONE IN CHLOROFORM—III

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INTRODUCTION

ABSTRACT. Ultrasonic velocities and adiabatic compressibilities have been determined of the solutions, ether-chloroform and acetone-chloroform. The compressibility-concentration curves lie below and above the straight lines for ideal mixtures in ether-chloroform and acetone-chloroform respectively. It is the first case, where ether and acetone have behaved oppositely with respect to chloroform. Previous work on these solutions in various other fields is sketched and combining the findings in these with the results on compressibilities, it is shown how in these solutions both hydrogen bonds and dipole associations are present, and how compressibility-determination is a method for finding which of the combinations, hydrogen bond or dipole association preponderates. In acetone-chloroform hydrogen bonds preponderate, while in ether-chloroform, dipole associations preponderate.

This paper is the third of the series on liquid mixtures.[1,2] The experimental technique and the basic considerations have been described in the first paper and will not be repeated here.

Ethers and ketones are known to form abnormal solutions with chloroform, with respect to solubility, heat of solution,[3] viscosity, dielectric polarisation, vapour pressure, volume contraction, etc. Both ethers and ketones behave similarly in respect of the above properties in chloroform and some sort of close relationship is supposed to be formed in the solution.

In our experiments, they behave absolutely in the opposite way, as will be evident from the graphs. In acetone-chloroform the compressibility-concentration curve lies above the straight line for the ideal case, and in the case of ether chloroform it lies appreciably below. This means that the intermolecular or inter-group forces in ether chloroform are enhanced while those in the other decreased as compared to the ideal case. This is a unique observation in that ethers and ketones have been observed to behave oppositely in chloroform.

EXPERIMENTAL RESULTS

The experimental technique and basic considerations relating compressibility to molecular interaction have been given in the first paper and will not be repeated here. The following are the results:

MIXTURE: ETHER-CHLOROFORM

Temp. = 27°.2C.

No.	Mole-fraction of ether	Density gm./cc.	Velocity m/s.	Compressibility (adiabtic) $\times 10^{-6}$ in bar^{-1}
1	0	1.466	984.7	70.3
2	.0665	1.429	981.5	72.6
3	.0792	1.398	977.4	75.0
4	.249	1.255	947.5	83.9
5	.328	1.181	975.2	89.0
6	.436	1.109	976.1	94.8
7	590	.996	978.1	105.0
8	·644	.955	976.8	109.7
9	.875	.795	980.0	131.0
10	1	7025	980.9	148.0

The velocity-concentration and compressibility-concentration curves are plotted in Fig. 1.

The velocity curve shows a well-defined minimum at mole-fraction of ether of .25.

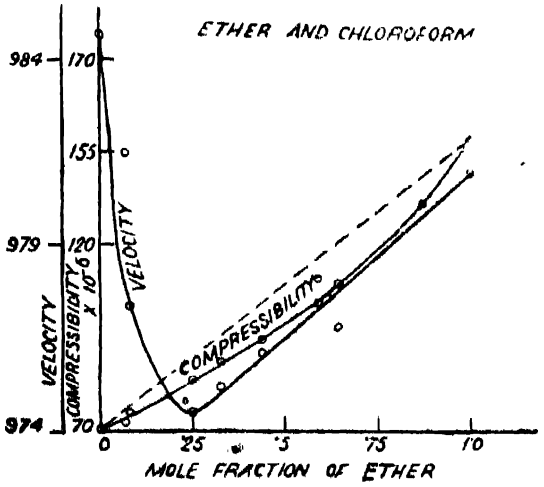

FIGURE 1

The compressibility curve always remains below the straight line corresponding to the ideal case.

MIXTURE : ACETONE-CHLOROFORM
Temp. = 27°.5C.

No.	Mole-fraction of acetone	Density gm./cc.	Velocity m /s.	Compressibility (adiabatic) $\times 10^{-6}$ in bar^{-1}
1	0	1.472	989	69.5
2	.109	1.403	994	72.2
3	.321	1.268	1009	77.5
4	.524	1 131	1037	82 2
5	.720	.991	1077	86.9
6	.909	.856	1139	90.1
7	1	.788	1183	90.7

The velocity-concentration and compressibility-concentration graphs are shown in Fig. 2.

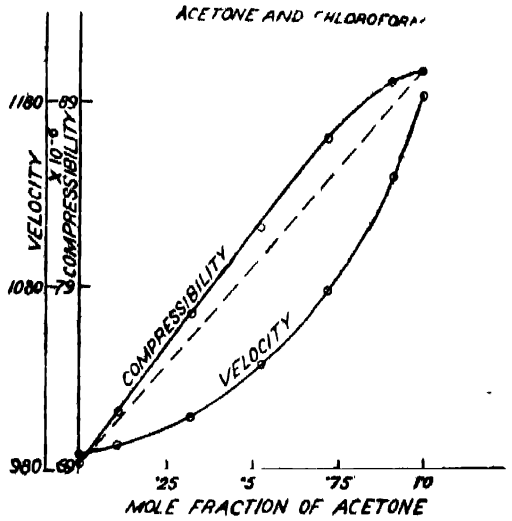

FIGURE 2

The velocity-curve remains below the straight line and compressibility-curve above the straight line corresponding to the ideal case.

From Figs. 1, 2, we gather the important fact that ether and acetone behave oppositely in chloroform with regard to compressibility of the solutions. In ether-chloroform the compressibility is less than that for the ideal case, and in acetone-chloroform the compressibility is greater than that for the ideal case.

It will be our purpose in the following to discuss and explain this opposite behaviour of ether and acetone.

Since this is the first case when acetone and ether behave oppositely in chloroform as against the numerous other properties where they act in the same way, we must go deep into the subject requiring full discussion.

DISCUSSION

The structure of molecules.—Acetone, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=O$ and ether, $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!O$ have the peculiarity, as is evident from the structural formulae, that the negative end of their dipoles, *i.e.*, O atoms are on the outside of the molecules while the positive ends are embedded inside or distributed. The forces of cohesion arising from dispersion, induction and dipole action are very short range forces, varying inversely as the sixth power of the distance. Further, the effectiveness of the contribution depends not so much upon the magnitude of the dipole moment as on its actual position with respect to the remaining part of the molecule. Dipoles, well-embedded in the molecule or distributed, have little action as compared to those on the outside. In the case of acetone and ether, the positive end being well-embedded inside, there will not be much dipole interaction energy between two molecules as compared to, say, the dispersion energy. For this reason, these liquids will be absolutely unassociated. This has been confirmed experimentally also, for example, by measuring their dielectric polarisation as a function of concentration when they are dissolved in some inert solvent like benzene or carbon tetrachloride.

Chloroform.—Chloroform, $\begin{matrix}Cl\\Cl\\Cl\end{matrix}\!\!>\!C-H$ has the dipole C—H and the three negative atoms Cl that are known for their electronegativity, *i.e.*, electron-attracting or proton-repelling power. Also these Cl atoms due to their polarisability polarise the C—H dipole. Now in the molecule of chloroform, as is evident from the structural formula the positive end H of the dipole is open to the surface.

Now, when acetone or ether is mixed with chloroform, the conditions become ideal for dipole action, the negative end O and positive end H, of dipoles of different molecules being on the surface. For this reason, the unlike molecules will be attracted to each other strongly and many abnormalities will arise in the properties of the solution as compared to the ideal case. Some sort of complex is supposed to be formed between the unlike molecules to explain the abnormalities. The question that has not been settled well, yet, is what is the exact nature of intermolecular relationship. Our compressibility data seem to decide the nature of the relationship.

In order to appreciate the light thrown by our compressibility data on the mode of behaviour of the solutions, it will be necessary to give experimental evidences of the existence of strong similar intermolecular action and the attempts that have been made in forming a suitable intermolecular picture on the basis of these data.

PREVIOUS EXPERIMENTAL EVIDENCES

Heat of mixing.—Macleod and Wilson studied the heat evolved when ether is mixed with chloroform in varying concentrations. The maximum heat is evolved at or very close to equimolecular proportions. This indicates that any complex formed might be having one molecule of ether and one of chloroform.

By applying the law of mass action, it was deduced that 14 to 20 per cent. of the molecules are mutually attached at 15°C. The method, however, lacks precision. A similar abnormal heat of solution is found in acetone-chloroform.

Partial pressures.—The solutions show large negative deviations from Raolt's law.[4,5] This shows that molecules are held together strongly in a complex, of whatever nature it may be, so that it is more difficult for molecules to evaporate in this state, than from an ideal solution. Dolezalek[7] concludes from the study of vapour pressures of ether and chloroform mixtures that at 19°C. about 24% of the molecules are combined. This is a slightly higher percentage than that deduced by Macleod and Wilson from heat of mixing.

Volume contraction on mixing.—There is a volume contraction of 1.25% for an equimolecular mixture of ether and chloroform. On the other hand, the volume contraction for acetone-chloroform is only .19%.[7] The wide difference between the two values is significant and will be discussed afterwards.

Solubility.—Zellhoefer, Copley and Marvel[8] measured the solubility of chloroform in ketones and ethers and found that ethers and ketones are highly soluble in chloroform, indicating strong intermolecular action. They investigated the effect of different forms of R_2O and R_2CO in CHX_3 on solubility, where R and X denote any radicals.

Dielectric polarisation.—Glasstone[9] observed that ethers and ketones have abnormal polarisation in tri-halogenomethanes. The abnormal polarisation must be attributed to the fact that the dipole moment of each constituent was greater than its usual value as a result of association with the other.

Infra-red absorption spectra.—Gordy[10] has observed the absorption spectra in solutions of chloroform and bromoform in various solvents including ketones, esters, ethers and amines. In the region of 4μ, a band has been observed which apparently is not characteristic of the spectrum of either the solute or the solvent. Because of the intensity of the band, it is thought to be a fundamental. Gordy thinks that the most reasonable interpretation is that it is an NH or OH vibration resulting from intermolecular hydrogen bond formation between the CH of chloroform and an N or O of the solvent. The band for the bromoform is weaker than that for the corresponding chloroform solutions.

Gordy[11] again remarks that although the spectra indicate the formation of hydrogen bonds in the manner suggested above, it is not absolutely necessary that they must combine in order to produce the absorption actually found. The

dielectric constant of the solution and other factors can probably also produce the results, the magnitude of which is extremely small.

DISCUSSION OF INTERMOLECULAR ACTION

From the above list of experimental evidence, there seems no doubt that there is strong intermolecular action, and now we wish to investigate the exact nature of the intermolecular process taking place.

Two probable pictures of intermolecular action have been proposed to account for the abnormal properties of the mixtures, and there has been a lot of discussion as to which of the two is in fact taking place. The two processes are as follows :

(*i*) Hydrogen bond formation

(*ii*) Dipole association.

Hydrogen bond.—The O of acetone or ether is supposed to donate two electrons to the H of chloroform, as is represented in the figure

$$CH_3CO \rightarrow HCCl_3.$$

Due to quantum mechanical consideration, there will be in fact a resonance as shown

$$(CH_3\dot{C}O \rightarrow H\bar{C}Cl_3) \rightleftharpoons (CH_3COH—CCl_3).$$

Dipole association.—In this case the H and O are attracted under their mutual fields, but there is no actual donation of the electrons. The dipole association may be represented in the figures as

$$\left(\overset{+\rightarrow}{CH_3CO} \quad \overset{+\rightarrow}{H\text{-}CCl_3} \right).$$

Glasstone[9] was the first to put forward the hypothesis of hydrogen bond formation from his studies on dielectric constants. There is a long discussion about hydrogen bond *versus* dipole association in his paper to which the reader may refer for greater details. Zellhoeffer, Copley and Marvel have discussed the problem from the solubility considerations to which also reference may be made.

Up till now the situation is that the experimental facts listed above can be explained on both the hypotheses, for both assume a great mutual attractive force between the unlike molecules through their different mechanisms. The usual tests of the hypotheses have been made by introducing electron-repelling or electron-attracting groups in the two molecules of chloroform, and of acetone or ether and then investigating the change in their mode of interaction.

On the hydrogen bond theory they are explained as due to their attraction or repulsion on the two electrons, thus affecting the tendency for donation, while the same results are explained equally well on the dipole association theory by involving the polarising action of those groups on the electrons

in question. These groups will alter the electron distribution of the respective bonds of chloroform and acetone in a way leading to a greater or less attraction between the unlike atoms, and thereby producing the observed effects.

There has been thus, so far, no critical criterion or observation which would show unambiguously the presence of one form of interaction or the other.

Now we shall show that our compressibility data are incomparably better in deciding for the mode of interaction. In the following we shall discuss the effect of hydrogen bond formation or dipole association on compressibility.

HYDROGEN BONDS AND COMPRESSIBILITY

The compressibility will increase on hydrogen bond formation and may be shown to be as follows :

As shown by Keesom and London, [11,12] the average cohesive energy over all positions between two dipoles of moments μ_1 and μ_2 at a distance R is

$$U = -\frac{2}{3} \cdot \frac{\mu_1^2 \mu_2^2}{R^6} \cdot \frac{1}{kT}$$

(k is Boltzmann's constant ; T, absolute temperature).

It has been shown [1] that compressibility behaves in the inverse way to the cohesive energy. In the to and fro motion in the liquid under ultrasonic waves, it is not one molecule which is the unit, but a whole associated structure, which may be composed of more than one molecule. Of course, when the molecules are free individuals, they singly form the units in the oscillating motion.

Now when the two unlike dipoles are at a distance from each other, there is cohesive energy among them as given by the above formula. The cohesive energy will increase rapidly as the distance still decreases. But when it becomes so little that the two molecules become a single unit through the hydrogen bond or otherwise, the cohesive energy between them, though very strong, gets ruled out from contributing to the decrease of compressibility concerned in the problem of sound propagation. Now it will be the cohesive energy between two such separate units, that we must consider for sound propagation.

As a hydrogen bond is formed, making two molecules as one close unit, the distance among the separate units will become greater than the distance that would have been between two free molecules in the absence of hydrogen bonds. As is clear from the above formula, the cohesive energy is very sensitive to distance, falling off as inverse of the sixth power of the distance. Hence this increase of distance on the formation of hydrogen bonds will lead to the increase of compressibility.

Besides, the dipoles in hydrogen bond will become effectively shielded for wielding any cohesive effect upon other units or molecules. It has already been shown how shielding of dipoles reduces the intermolecular activity of dipoles.

It has been found that compressibility of water decreases as its temperature rises, although the distance among the molecules is increasing due to thermal expansion. This is, no doubt, due to the breaking up of hydrogen bonds, which fact has been amply confirmed by infra-red and Raman spectra. Again in the mixture of water and alcohols, it has been shown that the decrease of compressibility from the ideal case is due to the breaking up of hydrogen bonds.

In a solution, therefore, the occurrence of hydrogen bonds will decrease the cohesive energy below the ideal value, or in other words, the compressibility curve will lie above the straight line corresponding to the ideal case (see acetone, chloroform).

COMPRESSIBILITY AND DIPOLE ASSOCIATION

In dipole association, there is no actual donation of electrons. The distance between the two molecules in dipole association is obviously greater than that when a hydrogen bond is formed, and the molecules vibrate as separate units in sound oscillations. This means that the strong cohesive energy between them is directly concerned in sound propagation, and the compressibility will therefore be much decreased. Again, in dipole association, there will not be a similar shielding as in the case of hydrogen bonds and the dipole activity will be present at all times as contrasted to the case of hydrogen bond. All these will lead to a lower value of compressibility than in the case of hydrogen bonds.

THE MIXTURE

In ether-chloroform, the compressibility is below the ideal value, while in acetone-chloroform, it is above the ideal value. The conclusions to be derived from the compressibility data, with regard to hydrogen bond *versus* dipole association theory, becomes self-evident in the light of what has been said before. They may be repeated as (1) in acetone-chloroform, hydrogen bonds are formed and (2) in ether chloroform, dipole associations are formed.

By examining the structure of acetone and ether molecules, it is quite easy to see why one type should prefer one way of coupling to the other. In acetone the C=O dipole has its 'O' absolutely unshielded by the rest of the molecule and its dipole moment is quite high (2 D). Both these factors are favourable for hydrogen bond formation. In ether on the other hand, the 'O' atom is relatively more shielded and the dipole moment is less (1.5 D). These may be taken as strong reasons why in acetone-chloroform hydrogen bonds are prevalent, while in ether-chloroform, the dipole associations.

Volume contraction.—The data on volume contraction on mixing support our findings. In ether-chloroform there is a larger contraction (1.25%) while in acetone-chloroform, a comparatively much smaller one.

In ether-chloroform, dipole associations being prevalent, there is high cohesional energy leading to this contraction, while in acetone-chloroform due to

the formation of hydrogen bonds, forces among units whether in the form of free molecules or bonded molecules, are much reduced; this will explain the experimental findings.

Vapour-pressure.—The data on vapour-pressure deviations can be explained quite easily on our views since in ether-chloroform mixture the escaping molecule has to overcome the attraction of its neighbouring dipole or dipoles, associated or free, while in the acetone-chloroform solution, it has to overcome the bond energy of its partner.

However, while keeping our main conclusions intact, we may accept a modified picture as well.

It can be seen that there is really no difference of kind but only of degree between hydrogen bonds and dipole association. When the H of chloroform and O of ether or acetone approach very near together under the action of electrostatic forces and random heat motion, conditions become favourable for the transfer of two electrons from the O atom, and a hydrogen bond may thereby be formed. When the two unlike molecules, on the other hand, are at a greater distance, it may not be possible for the transfer of electrons, but still it is a dipole association. Hence it seems that both dipole associations and hydrogen bonds are present, their relative preponderance depending upon the circumstances of the case.

So, in our actual case, we are led to the plausible conclusion that (1) Hydrogen bonds are preponderating in chloroform-acetone solution; (2) Dipole associations are preponderating in chloroform-ether solution.

Thus the determination of compressibilities is a new method of determining the nature of preponderance of the combinations between dipole associations or hydrogen bonds.

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